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(54) **Phosphonate additives for non-aqueous electrolyte in alkali metal electrochemical cells**

(57) An alkali metal, solid cathode, nonaqueous electrochemical cell capable of delivering high current pulses, rapidly recovering its open circuit voltage and having high current capacity, is described. The stated benefits are realized by the addition of at least one phos-

phonate additive to an electrolyte comprising an alkali metal salt dissolved in a mixture of a low viscosity solvent and a high permittivity solvent. A preferred solvent mixture includes propylene carbonate, dimethoxyethane and an alkyl phosphonate additive.

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Description

BACKGROUND OF INVENTION

5 1. Field of the Invention

[0001] The present invention generally relates to an alkali metal electrochemical cell, and more particularly, to an alkali metal cell suitable for current pulse discharge applications with reduced or no appreciable voltage delay. Still more particularly, the present invention relates to a lithium electrochemical cell activated with an electrolyte having an additive for the purpose of reducing and/or eliminating voltage delay under current pulse discharge applications. Voltage delay is a phenomenon typically exhibited in an alkali metal/transition metal oxide cell, and particularly, a lithium/silver vanadium oxide cell, that has been depleted of 40% to 70% of its capacity and is subjected to current pulse discharge applications. According to the present invention, the preferred additive to the activating electrolyte for such a chemistry is a phosphonate compound. A phosphite compound is another name for a phosphonate compound and is also preferred for the present invention.

[0002] The voltage response of a cell which does not exhibit voltage delay during the application of a short duration pulse or pulse train has distinct features. First, the cell potential decreases throughout the application of the pulse until it reaches a minimum at the end of the pulse, and second, the minimum potential of the first pulse in a series of pulses is higher than the minimum potential of the last pulse.

[0003] On the other hand, the voltage response of a cell which exhibits voltage delay during the application of a short duration pulse or during a pulse train can take one or both of two forms. One form is that the leading edge potential of the first pulse is lower than the end edge potential of the first pulse. In other words, the voltage of the cell at the instant the first pulse is applied is lower than the voltage of the cell immediately before the first pulse is removed. The second form of voltage delay is that the minimum potential of the first pulse is lower than the minimum potential of the last pulse when a series of pulses have been applied.

[0004] The initial drop in cell potential during the application of a short duration pulse reflects the resistance of the cell, i.e., the resistance due to the cathode-electrolyte interphase and the anode-electrolyte interphase and due to polarization. In the absence of voltage delay, the resistance due to passivated films on the anode and/or cathode is negligible. However, the formation of a surface film is unavoidable for alkali metal, and in particular, lithium metal anodes, and for lithium intercalated carbon anodes, due to their relatively low potential and high reactivity towards organic electrolytes. Thus, the ideal anode surface film should be electrically insulating and ionically conducting. While most alkali metal, and in particular, lithium electrochemical systems meet the first requirement, the second requirement is difficult to achieve. In the event of voltage delay, the resistance of these films is not negligible, and as a result, impedance builds up inside the cell due to this surface layer formation which often results in reduced discharge voltage and reduced cell capacity. In other words, the drop in potential between the background voltage and the lowest voltage under pulse discharge conditions, excluding voltage delay, is an indication of the conductivity of the cell, i.e., the conductivity of the cathode, anode, electrolyte, and surface films, while the gradual decrease in cell potential during the application of the pulse train is due to the polarization of the electrodes and electrolyte.

[0005] Thus, the existence of voltage delay is an undesirable characteristic of alkali metal/mixed metal oxide cells subjected to current pulse discharge conditions in terms of its influence on devices such as medical devices including implantable pacemakers and cardiac defibrillators. Voltage delay is undesirable because it limits the effectiveness and even the proper functioning of both the cell and the associated electrically powered device under current pulse discharge conditions.

45 2. Prior Art

[0006] One of the known solutions to the above problem is to saturate the electrolyte solution with carbon dioxide. CO₂-cycling efficiency is improved dramatically in secondary cell systems having a lithium anode activated with CO₂ saturated electrolytes (V.R. Koch and S.B. Brummer, *Electrochimica Acta*, 1978, 23, 55-62; U.S. Patent No. 4,853,304 to Ebner et al.; D. Aurbach, Y. Gofer, M. Ben-Zion and P. Aped, *J. Electroanal. Chem.* 1992, 339, 451-471). U.S. Patent No. 5,569,558 to Takeuchi et al. relates to the provision of a CO₂ saturated-electrolyte for alleviating the presence of voltage delay in primary cells having a mixed transition metal oxide cathode such as lithium/silver vanadium oxide cells. The same effect is also known for lithium intercalated carbon anode secondary batteries (D. Aurbach, Y. Ein-Eli, O. Chusid, Y. Carmeli, M. Babai and H. Yamin, *J. Electrochem. Soc.* 1994, 141, 603-611). Sulfur dioxide (SO₂) has also been reported to be another additive that improves charge-discharge cycling in rechargeable lithium ion cells (Y. Ein-Eli, S.R. Thomas and V.R. Koch, *J. Electrochem. Soc.* 1996, 143, L195-L197).

[0007] In spite of the success of CO₂ and SO₂ in improving cell discharge characteristics, their use has been limited. One problem associated with both CO₂ and SO₂ as electrolyte additives is that they are in a gaseous state at room

temperature, and are thus difficult to handle. Also, it is difficult to control the dissolved concentration of CO₂. Best results are achieved at pressures of up to 50 psig., which further detracts from the practicality of this additive.

[0008] Instead of carbon dioxide and sulfur dioxide, the present invention is directed to the provision of organic phosphonate or phosphite additives in the electrolyte of an alkali metal electrochemical cell to beneficially modify the anode surface film. The phosphonate additives are defined herein as organic mono-alkyl alkyl or dialkyl alkyl phosphonate compounds or phosphorous acid (phosphonic acid) provided as a co-solvent with commonly used organic aprotic solvents. The organic phosphite additives are in a condensed phase which makes them easy to handle in electrolyte preparation. When used as a co-solvent in an activating electrolyte, the phosphonate additives interact with the alkali metal anode to form an ionically conductive surface protective layer thereon. The conductive surface layer improves the discharge performance of the alkali metal electrochemical cell and minimizes or even eliminates voltage delay in the high current pulse discharge of such cells. Phosphonate compounds are sometimes referred to as phosphite compounds in the nomenclature, and the two names are used interchangeably throughout the specification.

SUMMARY OF THE INVENTION

[0009] The object of the present invention is to improve the pulse discharge performance of an alkali metal electrochemical cell, and more particularly a primary lithium electrochemical cell, by the provision of at least one of a family of phosphonate additives, preferably a mono-alkyl alkyl or dialkyl alkyl phosphonate compound, or phosphorous acid (phosphonic acid), as a co-solvent in the cell's activating nonaqueous electrolyte solution. Due to the high reduction potentials of the phosphonate group vs. lithium, the phosphonate additives compete effectively with the other electrolyte co-solvents or the solute to react with the lithium anode. Lithium phosphonate or the lithium salt of phosphonate reduction products are believed to be the major reaction products. These lithium salts are believed to deposit on the anode surface to form an ionically conductive protective film thereon. As a consequence, the chemical composition and perhaps the morphology of the anode surface protective layer is changed, and this proves beneficial to the discharge characteristics of the cell.

[0010] The thusly fabricated cell exhibits reduced or no appreciable voltage delay under current pulse discharge usage, which is an unexpected result. More particularly, the present invention is directed to the introduction of at least one phosphonate additive into the electrolyte of a lithium/silver vanadium oxide electrochemical cell for the purpose of reducing and/or eliminating voltage delay during pulse discharging applications. Alkali metal/transition metal oxide electrochemical systems are typically activated with an electrolyte comprising a relatively low viscosity solvent and a relatively high permittivity solvent. The solute of the electrolyte is an inorganic alkali metal salt wherein the alkali metal of the salt is the same as the alkali metal of the anode. The phosphonate compound of the present invention is introduced into the electrolyte as an additive to interact with the alkali metal anode, and particularly with the lithium anode, to form an ionically conductive protective anode surface layer which improves the discharge performance of the cell, and minimizes or even eliminates voltage delay in current pulse discharge conditions. Therefore, the present invention is directed to a novel electrolyte solution provided in operative association with an electrochemical system incorporated into a defibrillator battery to minimize or even eliminate voltage delay under high current pulse discharge conditions.

[0011] These and other objects of the present invention will become increasingly more apparent to those skilled in the art by reference to the following description.

DETAILED DESCRIPTION OF THE PREFERRED EIMBODIMENTS

[0012] As used herein, the term "pulse" means a short burst of electrical current of a significantly greater amplitude than that of a prepulse current immediately prior to the pulse. A pulse train consists of at least two pulses of electrical current delivered in relatively short succession with or without open circuit rest between the pulses.

[0013] The electrochemical cell of the present invention includes an anode selected from Groups IA, IIA or IIIB of the Periodic Table of Elements, including lithium, sodium, potassium, etc., and their alloys and intermetallic compounds including, for example Li-Si, Li-B and Li-Si-B alloys and intermetallic compounds. The preferred anode comprises lithium, and the more preferred anode comprises a lithium alloy, the preferred lithium alloy being a lithium-aluminum alloy. The greater the amount of aluminum present by weight in the alloy, however the lower the energy density of the cell.

[0014] The form of the anode may vary, but preferably the anode is a thin metal sheet or foil of the anode metal, pressed or rolled on a metallic anode current collector, i.e., preferably comprising nickel, to form an anode component. In the exemplary cell of the present invention, the anode component has an extended tab or lead of the same material as the anode current collector, i.e., preferably nickel, integrally formed therewith such as by welding and contacted by a weld to a cell case of conductive metal in a case-negative electrical configuration. Alternatively, the anode may be formed in some other geometry, such as a bobbin shape, cylinder or pellet to allow an alternate low surface cell design.

[0015] The cathode is preferably of a solid material and the electrochemical reaction at the cathode involves con-

version of ions which migrate from the anode to the cathode in atomic or molecular forms. The solid cathode material may comprise a metal, a metal oxide, a mixed metal oxide, a metal sulfide or a carbonaceous compound, and combinations thereof. The metal oxide, the mixed metal oxide and the metal sulfide can be formed by the chemical addition, reaction, or otherwise intimate contact of various metal oxides, metal sulfides and/or metal elements, preferably during thermal treatment, sol-gel formation, chemical vapor deposition or hydrothermal synthesis in mixed states. The active materials thereby produced contain metals, oxides and sulfides of Groups IB, IIB, IIIB, IVB, VB, VIB, VIIB and VIII, which includes the noble metals and/or other oxide and sulfide compounds.

[0016] One preferred mixed metal oxide has the general formula $SM_xV_2O_y$, wherein SM is a metal selected from Groups IB to VIIB and VIII of the Periodic Table of Elements, wherein x is about 0.30 to 2.0 and y is about 4.5 to 6.0 in the general formula. By way of illustration, and in no way intended to be limiting, one exemplary cathode active material comprises silver vanadium oxide (SVO) having the general formula $Ag_xV_2O_y$ in any one of its many phases, i.e., β -phase silver vanadium oxide having in the general formula $x = 0.35$ and $y = 5.8$, γ -phase silver vanadium oxide having in the general formula $x = 0.74$ and $y = 5.37$ and ϵ -phase silver vanadium oxide having in the general formula $x = 1.0$ and $y = 5.5$, and combination and mixtures of phases thereof. For a more detailed description of such a cathode active material reference is made to U.S. Patent No. 4,310,609 to Liang et al., which is assigned to the assignee of the present invention and incorporated herein by reference.

[0017] Another preferred composite cathode active material includes V_2O_z wherein $z \leq 5$ combined with Ag_2O with the silver in either the silver(II), silver(I) or silver(0) oxidation state and CuO with the copper in either the copper(II), copper(I) or copper(0) oxidation state to provide the mixed metal oxide having the general formula $Cu_xAg_yV_2O_z$, (CS-VO). Thus, this composite cathode active material may be described as a metal oxide-metal oxide-metal oxide, a metal-metal oxide-metal oxide, or a metal-metal-metal oxide and the range of material compositions found for $Cu_xAg_yV_2O_z$ is preferably about $0.01 \leq x \leq 1.0$, about $0.01 \leq y \leq 1.0$ and about $5.01 \leq z \leq 6.5$. Typical forms of CSVO are $Cu_{0.16}Ag_{0.67}V_2O_z$ with z being about 5.5 and $Cu_{0.5}Ag_{0.5}V_2O_z$ with z being about 5.75. The oxygen content is designated by z since the exact stoichiometric proportion of oxygen in CSVO can vary depending on whether the cathode material is prepared in an oxidizing atmosphere such as air or oxygen, or in an inert atmosphere such as argon, nitrogen and helium. For a more detailed description of this cathode active material reference is made to U.S. Patent Nos. 5,472,810 to Takeuchi et al. and 5,516,340 to Takeuchi et al., both of which are assigned to the assignee of the present invention and incorporated herein by reference.

[0018] Additional cathode active materials include manganese dioxide, lithium cobalt oxide, lithium nickel oxide, copper vanadium oxide, titanium disulfide, copper oxide, copper sulfide, iron sulfide, iron disulfide, and fluorinated carbon, and mixtures thereof. Preferably, the cathode comprises from about 80 to about 99 weight percent of the cathode active material.

[0019] Cathode active materials prepared as described above are preferably mixed with a binder material such as a powdered fluoro-polymer, more preferably powdered polytetrafluoroethylene or powdered polyvinylidene fluoride present at about 1 to about 5 weight percent of the cathode mixture. Further, up to about 10 weight percent of a conductive diluent is preferably added to the cathode mixture to improve conductivity. Suitable materials for this purpose include acetylene black, carbon black and/or graphite or a metallic powder such as powdered nickel, aluminum, titanium and stainless steel. The preferred cathode active mixture thus includes a powdered fluoro-polymer binder present at about 3 weight percent, a conductive diluent present at about 3 weight percent and about 94 weight percent of the cathode active material. The cathode active mixture may be in the form of one or more plates operatively associated with at least one or more plates of anode material, or in the form of a strip wound with a corresponding strip of anode material in a structure similar to a "jellyroll".

[0020] In order to prevent internal short circuit conditions, the cathode is separated from the Group IA, IIA or IIIB anode material by a suitable separator material. The separator is of electrically insulative material, and the separator material also is chemically unreactive with the anode and cathode active materials and both chemically unreactive with and insoluble in the electrolyte. In addition, the separator material has a degree of porosity sufficient to allow flow therethrough of the electrolyte during the electrochemical reaction of the cell. Illustrative separator materials include woven and non-woven fabrics of polyolefinic fibers or fluoropolymeric fibers including polyvinylidene fluoride, polyethylenetetrafluoroethylene, and polyethylenetrifluoroethylene laminated or superposed with a polyolefinic or a fluoropolymeric microporous film. Suitable microporous films include a polytetrafluoroethylene membrane commercially available under the designation ZITEX (Chemplast Inc.), polypropylene membrane commercially available under the designation CELGARD (Celanese Plastic Company, Inc.) and a membrane commercially available under the designation DEXIGLAS (C.H. Dexter, Div., Dexter Corp.). The separator may also be composed of non-woven glass, glass fiber materials and ceramic materials.

[0021] The form of the separator typically is a sheet which is placed between the anode and cathode electrodes and in a manner preventing physical contact therebetween. Such is the case when the anode is folded in a serpentine-like structure with a plurality of cathode plates disposed intermediate the anode folds and received in a cell casing or when the electrode combination is rolled or otherwise formed into a cylindrical "jellyroll" configuration.

[0022] The electrochemical cell of the present invention further includes a nonaqueous, ionically conductive electrolyte operatively associated with the anode and the cathode electrodes. The electrolyte serves as a medium for migration of ions between the anode and the cathode during the electrochemical reactions of the cell and nonaqueous solvents suitable for the present invention are chosen so as to exhibit those physical properties necessary for ionic transport (low viscosity, low surface tension and wettability). Suitable nonaqueous solvents are comprised of an inorganic salt dissolved in a nonaqueous solvent and more preferably an alkali metal salt dissolved in a mixture of aprotic organic solvents comprising a low viscosity solvent including organic esters, ethers and dialkyl carbonates, and mixtures thereof, and a high permittivity solvent including cyclic carbonates, cyclic esters and cyclic amides, and mixtures thereof. Low viscosity solvents include tetrahydrofuran (THF), diisopropylether, methyl acetate (MA), diglyme, triglyme, tetraglyme, 1,2-dimethoxyethane (DME), 1,2-diethoxyethane (DEE), 1-ethoxy,2-methoxyethane (EME), dimethyl carbonate (DMC), diethyl carbonate (DEC), dipropyl carbonate (DPC), ethyl methyl carbonate (EMC), methyl propyl carbonate (MPC) and ethyl propyl carbonate (EPC), and mixtures thereof. High permittivity solvents include propylene carbonate (PC), ethylene carbonate (EC), butylene carbonate (BC), acetonitrile, dimethyl sulfoxide, dimethyl formamide, dimethyl acetamide, γ -butyrolactone (GBL) and N-methyl-pyrrolidinone (NMP), and mixtures thereof.

[0023] The preferred electrolyte comprises an inorganic alkali metal salt, and in the case of an anode comprising lithium, the alkali metal salt of the electrolyte is a lithium based salt. Known lithium salts that are useful as a vehicle for transport of alkali metal ions from the anode to the cathode include LiPF_6 , LiBF_4 , LiAsF_6 , LiSbF_6 , LiClO_4 , LiAlCl_4 , LiGaCl_4 , $\text{Li}(\text{SO}_2\text{CF}_3)_3$, $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, LiSCN , $\text{LiO}_3\text{SCF}_2\text{CF}_3$, $\text{LiC}_6\text{F}_5\text{SO}_3$, LiO_2CF_3 , LiSO_3F , $\text{LiB}(\text{C}_6\text{H}_5)_4$ and LiCF_3SO_3 , and mixtures thereof. Suitable salt concentrations typically range between about 0.8 to 1.5 molar, and a preferred electrolyte for a lithium/transition metal oxide electrochemical cell includes LiAsF_6 or LiPF_6 dissolved in a 50:50 mixture, by volume, of PC and DME.

[0024] In accordance with the present invention, at least one organic phosphonate additive is provided as a co-solvent in the electrolyte solution of the previously described alkali metal electrochemical cell. The phosphonate additive is preferably an alkyl phosphonate compound having the general formula $(\text{R}^1\text{O})\text{P}(=\text{O})(\text{OR}^2)(\text{R}^3)$ wherein R^1 , R^2 and R^3 are the same or different, and they can be a hydrogen atom or a saturated or unsaturated organic group containing 1 to 13 carbon atoms. The greatest effect is found when dimethyl phosphonate, diethyl phosphonate, dipropyl phosphonate, dibutyl phosphonate, diphenyl phosphonate, dibenzyl phosphonate, dimethyl methylphosphonate, diethyl methylphosphonate, dipropyl methylphosphonate, dibutyl methylphosphonate, diphenyl methylphosphonate, dibenzyl methylphosphonate, dimethyl benzylphosphonate, ethyl methylphosphonate, dimethyl diphenylmethylphosphonate and phosphorous acid or phosphonic acid, and mixtures thereof are used as additives in the electrolyte.

[0025] The above described compounds are only intended to be exemplary of those that are useful with the present invention, and are not to be construed as limiting. Those skilled in the art will readily recognize phosphonate compounds which come under the purview of the general formula set forth above and which will be useful as additives for the electrolyte to reduce voltage delay according to the present invention.

[0026] While not intending to be bound by any particular mechanism, it is believed that due to the presence of the $\text{P}=\text{O}$ bond in the $-\text{OP}(=\text{O})(\text{R})\text{O}-$ functional group, the bond between oxygen and at least one of the group R^1 and R^2 is severed and the phosphonate intermediate is able to compete effectively with the other electrolyte solvents or solutes to react with lithium and form a phosphonate salt, i.e., lithium phosphonate, or the lithium salt of a phosphonate reduction product on the surface of the anode. The resulting salt is more conductive than lithium oxide which may form on the anode in the absence of the organic phosphonate additive. As a consequence, the chemical composition and perhaps the morphology of the anode surface protective layer is believed to be changed with concomitant benefits to the cell's discharge characteristics.

[0027] In the present invention, the anode is lithium metal and the cathode is preferably the transition mixed metal oxide $\text{AgV}_2\text{O}_{5.5}$ (SVO). The preferred electrolyte is 1.0M to 1.2M LiAsF_6 dissolved in an aprotic solvent mixture comprising at least one of the above listed low viscosity solvents and at least one of the above listed high permittivity solvents. The preferred aprotic solvent mixture comprises a 50/50, by volume, mixture of propylene carbonate and dimethoxyethane. The concentration of the above discussed phosphonate additives according to the present invention should preferably be in the range of between about 0.001M to about 0.20M. The positive effects of these additives in reducing voltage delay in a pulse discharging alkali metal cell have been achieved both at room temperature as well as at temperatures up to about 37°C. This makes the novel electrolyte solution of the present invention particularly useful for activating an alkali metal/transition metal oxide cell incorporated into an implantable medical device such as a cardiac defibrillator to minimize or even eliminate voltage delay under high current pulse discharge conditions.

[0028] As is well known by those skilled in the art, an implantable cardiac defibrillator is a device that requires a power source for a generally medium rate, constant resistance load component provided by circuits performing such functions as, for example, the heart sensing and pacing functions. From time to time, the cardiac defibrillator may require a generally high rate, pulse discharge load component that occurs, for example, during charging of a capacitor in the defibrillator for the purpose of delivering an electrical shock to the heart to treat tachyarrhythmias, the irregular, rapid heartbeats that can be fatal if left uncorrected. Reduction and even elimination of voltage delay during a current

pulse application is important for proper device operation and extended device life.

[0029] The assembly of the cell described herein is preferably in the form of a wound element cell. That is, the fabricated cathode, anode and separator are wound together in a "jellyroll" type configuration or "wound element cell stack" such that the anode is on the outside of the roll to make electrical contact with the cell case in a case-negative configuration. Using suitable top and bottom insulators, the wound cell stack is inserted into a metallic case of a suitable size dimension. The metallic case may comprise materials such as stainless steel, mild steel, nickel-plated mild steel, titanium, tantalum or aluminum, but not limited thereto, so long as the metallic material is compatible for use with components of the cell.

[0030] The cell header comprises a metallic disc-shaped body with a first hole to accommodate a glass-to-metal seal/terminal pin feedthrough and a second hole for electrolyte filling. The glass used is of a corrosion resistant type having up to about 50% by weight silicon such as CABAL 12, TA 23 or FUSITE 425 or FUSITE 435. The positive terminal pin feedthrough preferably comprises titanium although molybdenum, aluminum, nickel alloy, or stainless steel can also be used. The cell header comprises elements having compatibility with the other components of the electrochemical cell and is resistant to corrosion. The cathode lead is welded to the positive terminal pin in the glass-to-metal seal and the header is welded to the case containing the electrode stack. The cell is thereafter filled with the electrolyte solution comprising at least one of the phosphonate additives described hereinabove and hermetically sealed such as by close-welding a stainless steel ball over the fill hole, but not limited thereto.

[0031] The above assembly describes a case-negative cell, which is the preferred construction of the exemplary cell of the present invention. As is well known to those skilled in the art, the exemplary electrochemical system of the present invention can also be constructed in a case-positive configuration.

[0032] The following examples describe the manner and process of an electrochemical cell according to the present invention, and set forth the best mode contemplated by the inventors of carrying out the invention, but are not construed as limiting.

EXAMPLE I

[0033] Lithium anode material was pressed on nickel current collector screen and silver vanadium oxide cathode material was pressed on titanium current collector screen. A prismatic cell stack assembly configuration with two layers of microporous membrane propylene separator sandwiched between the anode and cathode was prepared. The electrode assembly was then hermetically sealed in a stainless steel casing in a case-negative configuration. Three cells were activated with the standard electrolyte consisting of 1.0M LiAsF₆ dissolved in a 50:50, by volume, mixture of PC and DME without an organic phosphonate additive (Group 1). Fifteen additional cells (three cells per group) were activated with the same electrolyte used to activate the Group 1 cells and further containing 0.005M, 0.01M, 0.05M, 0.10M, or 0.20M of dimethyl methylphosphonate (DMMP), as set forth in Table 1.

Table 1

Cell Construction			
Group	[LiAsF ₆]	PC:DME	[DMMP]
1	1.0M	50:50	0.00M
2	1.0M	50:50	0.005M
3	1.0M	50:50	0.01M
4	1.0M	50:50	0.05M
5	1.0M	50:50	0.10M
6	1.0M	50:50	0.20M

[0034] A constant resistive load of 2.49 k Ω was applied to all eighteen cells for 17 hours during an initial predischage burn-in period. The predischage period is referred to as burn-in and depleted the cells of approximately 1% of their theoretical capacity. Following burn-in, the cells were subjected to acceptance pulse testing consisting of four 10 second pulses (23.2 mA/cm²) with a 15 second rest between each pulse. The average discharge readings for the pre-pulse potentials, voltage delay and pulse minimum potentials during acceptance pulse testing for these pulse trains are summarized in Table 2.

Table 2

Acceptance Pulse Train Voltages (average)				
Group	Ppre1	V-Delay	P1min	P4min
1	3.261	0.388	2.145	2.508
2	3.262	0.254	2.331	2.534
3	3.264	0.277	2.316	2.539
4	3.268	0.274	2.312	2.529
5	3.271	0.273	2.306	2.520
6	3.271	0.250	2.340	2.529

[0035] The data in Table 2 clearly demonstrate the beneficial effect that the phosphonate additive has on voltage delay in a pulse discharging electrochemical cell. All groups of cells had similar pre-pulse potentials and all of the cells exhibited at least some voltage delay during acceptance pulse testing. Voltage delay is calculated as pulse 1 end potential minus pulse 1 minimum potential. The trend is that during acceptance pulse testing the greater the DMMP concentration, the smaller the voltage delay. However, the pulse 1 minimum potentials and the pulse 4 minimum potentials for the respective pulse trains showed a maximum average voltage at DMMP concentrations of 0.20M and 0.01M, respectively. At DMMP concentrations greater than about 0.20M, the pulse minimum potentials decreased as a result of increasing DMMP concentrations during acceptance pulse testing.

[0036] Following acceptance pulse testing, all of the cells were discharged under loads of 9.53 kohm with superimposed pulse trains applied every 39 days. The pulse trains consisted of four 23.2 mA/cm², 10 second pulses with 15 seconds rest between each pulse. The average discharge reading for the pre-pulse potentials, voltage delay and pulse minimum potentials for pulse trains 1 to 6 as summarized in Tables 3 to 8, respectively.

Table 3

Pulse Train 1 Voltages (average)					
Group	[DMMP]	Ppre1	V-Delay	P1min	P4min
1	0.00M	3.227	0.000	2.638	2.513
2	0.005M	3.223	0.000	2.649	2.531
3	0.01M	3.223	0.000	2.654	2.540
4	0.05M	3.224	0.000	2.636	2.533
5	0.10M	3.224	0.000	2.637	2.526
6	0.20M	3.240	0.000	2.627	2.515

Table 4

Pulse Train 2 Voltages (average)					
Group	[DMMP]	Ppre1	V-Delay	P1min	P4min
1	0.00M	3.172	0.000	2.578	2.412
2	0.005M	3.166	0.000	2.591	2.432
3	0.01M	3.165	0.000	2.589	2.435
4	0.05M	3.162	0.000	2.553	2.410
5	0.10M	3.161	0.000	2.537	2.395
6	0.20M	3.161	0.000	2.517	2.378

Table 5

Pulse Train 3 Voltages (average)					
Group	[DMMP]	Ppre1	V-Delay	P1min	P4min
1	0.00M	2.882	0.000	2.358	2.244
2	0.005M	2.876	0.001	2.375	2.265

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Table 5 (continued)

Pulse Train 3 Voltages (average)					
Group	[DMMP]	Ppre1	V-Delay	P1min	P4min
3	0.01M	2.875	0.000	2.375	2.271
4	0.05M	2.875	0.000	2.365	2.265
5	0.10M	2.871	0.000	2.355	2.258
6	0.20M	2.876	0.000	2.339	2.249

Table 6

Pulse Train 4 Voltages (average)					
Group	[DMMP]	Ppre1	V-Delay	P1min	P4min
1	0.00M	2.598	0.058	2.073	2.113
2	0.005M	2.593	0.063	2.082	2.131
3	0.01M	2.593	0.070	2.081	2.141
4	0.05M	2.594	0.076	2.084	2.144
5	0.10M	2.590	0.098	2.064	2.138
6	0.20M	2.597	0.123	2.031	2.122

Table 7

Pulse Train 5 Voltages (average)					
Group	[DMMP]	Ppre1	V-Delay	P1min	P4min
1	0.00M	2.533	0.125	1.621	1.770
2	0.005M	2.532	0.161	1.637	1.835
3	0.01M	2.529	0.160	1.652	1.847
4	0.05M	2.529	0.207	1.644	1.874
5	0.10M	2.527	0.234	1.624	1.865
6	0.20M	2.528	0.217	1.650	1.870

Table 8

Pulse Train 6 Voltage (average)					
Group	[DMMP]	Ppre1	V-Delay	P1min	P4min
1	0.00M	2.488	0.000	1.715	1.576
2	0.005M	2.485	0.000	1.811	1.692
3	0.01M	2.484	0.000	1.786	1.678
4	0.05M	2.487	0.002	1.782	1.722
5	0.10M	2.478	0.000	1.747	1.665
6	0.20M	2.482	0.003	1.734	1.669

[0037] During pulse discharge testing, all cells had similar prepulse potentials and, in pulse trains 1 to 3, none of the cells exhibited voltage delay. Groups 2 to 4 cells with relatively low DMMP concentrations presented similar or higher pulse minimum potentials than that of the control cells. For the groups 5 and 6 cells having the greater DMMP concentrations, similar or lower pulse minimum potentials were present relative to that of the control cells.

[0038] In pulse trains 4 and 5, all cells exhibited voltage delay. Cells with the DMMP additive exhibited larger voltage delay than that of the control cells. The trend is that the greater the DMMP concentration, the larger the voltage delay. However, in pulse train 4, all of the cells with the DMMP additive exhibited higher pulse 4 minimum potentials than that of the control cells. In addition, in pulse train 5, all cells with the DMMP additive had higher pulse 1 and pulse 4 minimum potentials than that of the control cells.

[0039] In pulse train 6, all of the cells showed no voltage delay. Again, all cells having the DMMP additive presented greater pulse minimum potentials than that of the control cells.

EXAMPLE II

[0040] Eighteen cells were constructed in a similar manner as those described in Example I except for the alkyl phosphonate additive. Specifically, three of the cells were activated with the standard electrolyte consisting of 1.0M LiAsF₆ dissolved in a 50:50, by volume, mixture of PC and DME without an organic phosphonate additive (Group 1). Fifteen cells (three cells per group) were activated with the same electrolyte used to activate the Group 1 cells and further containing 0.005M, 0.01M, 0.05M, 0.10M, or 0.20M of dibenzyl phosphonate or dibenzyl phosphite (DBPI).

[0041] In a similar manner as the cells discharged in Example I, a constant resistive load of 2.49 k Ω was applied to all of the cells for 17 hours during an initial predischARGE burn-in period. Following burn-in, the cells were subjected to acceptance pulse testing consisting of four 10 second pulses (23.2 mA/cm²) with a 15 second rest between each pulse. The averaged discharge readings for the pre-pulse potentials, voltage delay and pulse minimum potentials during acceptance pulse testing for these pulse trains are summarized in Table 9.

Table 9

Acceptance Pulse Train Voltages (average)					
Group	[DBPI]	Ppre1	V-Delay	P1min	P4min
1	0.00M	3.245	0.225	2.335	2.490
2	0.005M	3.270	0.078	2.484	2.506
3	0.01M	3.270	0.040	2.516	2.503
4	0.05M	3.270	0.016	2.455	2.403
5	0.10M	3.267	0.071	2.377	2.365
6	0.20M	3.273	0.043	2.385	2.355

[0042] All of the cells having the DBPI additives exhibited lesser voltage delay and greater pulse 1 minimum potentials than that of the control cells during acceptance pulse testing. Group 2 and 3 cells also exhibited slightly greater pulse 4 minimum potentials than that of the control cells. However, for cells with greater DBPI concentrations, the pulse 4 minimum potentials were lower than that of the control cells.

[0043] Following acceptance pulse testing, all of the cells were discharged under loads of 9.53 kohm with superimposed pulse trains applied every 39 days. The pulse trains consisted of four 23.2 mA/cm², 10 second pulses with 15 seconds rest between each pulse. The average discharge reading for the pre-pulse potentials, voltage delay and pulse minimum potentials for pulse train 1 to 5 are summarized in Tables 10 to 14, respectively.

Table 10

Pulse Train 1 Voltages (average)					
Group	[DBPI]	Ppre1	V-Delay	P1min	P4min
1	0.00M	3.215	0.000	2.600	2.477
2	0.005M	3.222	0.000	2.579	2.472
3	0.01M	3.222	0.000	2.579	2.471
4	0.05M	3.229	0.000	2.506	2.384
5	0.10M	3.227	0.000	2.487	2.348
6	0.20M	3.236	0.001	2.493	2.357

Table 11

Pulse Train 2 Voltages (average)					
Group	[DBPI]	Ppre1	V-Delay	P1min	P4min
1	0.00M	3.161	0.000	2.529	2.389
2	0.005M	3.164	0.000	2.486	2.359
3	0.01M	3.162	0.000	-2.487	2.361

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Table 11 (continued)

Pulse Train 2 Voltages (average)					
Group	[DBPI]	Ppre1	V-Delay	P1min	P4min
4	0.05M	3.156	0.000	2.426	2.297
5	0.10M	3.141	0.000	2.390	2.265
6	0.20M	3.127	0.000	2.377	2.259

Table 12

Pulse Train 3 Voltages (average)					
Group	[DBPI]	Ppre1	V-Delay	P1min	P4min
1	0.00M	2.874	0.000	2.454	2.267
2	0.005M	2.884	0.000	2.337	2.250
3	0.01M	2.882	0.001	2.334	2.242
4	0.05M	2.874	0.000	2.282	2.201
5	0.10M	2.857	0.001	2.238	2.162
6	0.20M	2.852	0.000	2.196	2.131

Table 13

Pulse Train 4 Voltages (average)					
Group	[DBPI]	Ppre1	V-Delay	P1min	P4min
1	0.00M	2.593	0.049	2.112	2.132
2	0.005M	2.599	0.000	2.183	2.118
3	0.01M	2.595	0.001	2.176	2.108
4	0.05M	2.592	0.000	2.137	2.034
5	0.10M	2.588	0.001	2.092	1.988
6	0.20M	2.571	0.000	2.032	1.937

Table 14

Pulse Train 5 Voltages (average)					
Group	[DBPI]	Ppre1	V-Delay	P1min	P4min
1	0.00M	2.532	0.079	1.826	1.912
2	0.005M	2.535	0.004	1.988	1.975
3	0.01M	2.533	0.001	2.070	2.017
4	0.05M	2.533	0.002	2.033	1.962
5	0.10M	2.536	0.000	1.971	1.894
6	0.20M	2.529	0.002	1.925	1.836

[0044] In pulse trains 1 to 3, no voltage delay was observed for any of the cells. Group 1 control cells presented the greatest pulse minimum potentials among all of the group of cells. The trend is that the higher the DBPI concentration, the lower the pulse minimum potentials for the various cell groups.

[0045] In pulse trains 4 and 5, only the group 1 control cells exhibited significant voltage delay. All of the cells with the DBPI additive exhibited no voltage delay. The group 2 to 4 cells with the low DBPI concentrations always exhibited greater pulse minimum potentials than that of the group 1 cells. While the groups 5 and 6 cells with relatively high DBPI concentrations had lower P1 minimum and P4 minimum potentials than that of the group 1 cells in pulse train 4, they exhibited higher P1 minimum potentials than the group 1 cells in pulse train 5, although their P4 minimum potentials were still lower than that of the group 1 cells.

[0046] While not intended to be bound by any particular theory, it is believed that at phosphonate additive concen-

trations greater than about 0.20M for DMMP and about 0.01M for DBPI, the thickness of the anode surface film, composed of the reduction products of the phosphonate additive and the electrolyte, may increase which results in increased internal resistance. Since alkyl phosphonate additives are believed to have relatively high viscosity constants, the presence of a high phosphonate additive concentration may also lower the overall electrolyte conductivity. Thus, the choice of phosphonate additive concentration is believed to be important. The concentration limit is between about 0.001M to 0.20M. The beneficial effect of the alkyl phosphonate will not be apparent if the additive concentration is less than about 0.001M. On the other hand, if the additive concentration is greater than about 0.20M, the beneficial effect of the additive will be cancelled by the detrimental effect of higher internal cell resistance due to the thicker anode surface film formation and lower electrolyte conductivity.

[0047] Thus, the existence of voltage delay is due to the formation of an anode surface passivation layer that is ionically less conductive than either the anode material itself or the electrolyte solution. In the presence of an alkyl phosphonate additive or phosphorous acid according to the present invention, the anode passivation layer is chemically modified to be ionically more conductive than the passivation layer formed without the benefit of the organic phosphonate additive. It is believed that due to the presence of the -OP(=O)(R)O- functional group, the reductive cleavage of at least one of the OR^1 and OR^2 bonds in the phosphonate additives of the present invention may produce lithium phosphonate or the lithium salt of a phosphonate reduction product on the anode surface. This surface film is ionically more conductive than the film formed in the absence of the additives and it is responsible for the increased cell performance, especially during pulse discharge applications. As a consequence, diminished voltage delay results when an alkali metal/transition metal oxide couple activated with a nonaqueous organic solvent having a phosphonate additive dissolved therein according to the present invention is subjected to a pulse discharge application.

[0048] It is appreciated that various modifications to the inventive concepts described herein may be apparent to those of ordinary skill in the art without departing from the spirit and scope of the present invention as defined by the appended claims.

Claims

1. An electrochemical cell which is dischargeable to deliver a current pulse while exhibiting reduced voltage delay, which comprises:

- a) an anode comprising an alkali metal;
- b) a solid cathode of electrically conductive material; and
- c) a nonaqueous electrolyte activating the anode and the cathode, the nonaqueous electrolyte comprising:
 - i) a first solvent selected from the group consisting of an ester, an ether and a dialkyl carbonate, and mixtures thereof;
 - ii) a second solvent selected from the group consisting of a cyclic carbonate, a cyclic ester and a cyclic amide, and mixtures thereof;
 - iii) a phosphonate additive; and
 - iv) an alkali metal salt dissolved therein, wherein the alkali metal of the salt is similar to the alkali metal comprising the anode, and wherein the activated anode and cathode provide the electrochemical cell dischargeable to deliver at least one current pulse of a short duration burst of electrical current of a significantly greater amplitude than that of a prepulse current immediately prior to the pulse such that the pulse one end potential minus the pulse one minimum potential is less than about 0.3 volts.

2. The electrochemical cell according to Claim 1 wherein the phosphonate additive has the formula: $(\text{R}^1\text{O})\text{P(=O)}(\text{OR}^2)(\text{R}^3)$, and wherein R^1 , R^2 and R^3 are the same or different and they can be a hydrogen atom or a saturated or unsaturated organic group containing 1 to 13 carbon atoms.

3. The electrochemical cell according to Claim 1 or Claim 2 wherein the dialkyl phosphonate is selected from dimethyl phosphonate, diethyl phosphonate, dipropyl phosphonate, dibutyl phosphonate, diphenyl phosphonate, dibenzyl phosphonate, dimethyl methylphosphonate, diethyl methylphosphonate, dipropyl methylphosphonate, dibutyl methylphosphonate, diphenyl methylphosphonate, dibenzyl methylphosphonate, dimethyl benzylphosphonate, ethyl methylphosphonate, dimethyl diphenylmethylphosphonate, phosphorous acid, phosphonic acid or mixtures thereof.

4. The electrochemical cell according to any one of Claims 1 to 3 wherein the phosphonate additive is present in the electrolyte in a range of about 0.001M to about 0.20M.

5. The electrochemical cell according to any one of Claims 1 to 4 wherein the phosphonate additive is dimethyl methylphosphonate present in the electrolyte at a concentration of about 0.20M.
- 5 6. The electrochemical cell according to any one of Claims 1 to 4 wherein the phosphonate additive is dibenzyl phosphonate present in the electrolyte at a concentration of about 0.01M.
7. The electrochemical cell according to any one of Claims 1 to 6 wherein there are least two pulses delivered in succession with or without an open circuit period between the pulses.
- 10 8. The electrochemical cell according to Claim 7 wherein the current pulses are of about 23.2 mA/cm².
9. The electrochemical cell according to any one of Claims 1 to 8 wherein the first solvent is selected from tetrahydrofuran, diisopropylether, methyl acetate, diglyme, triglyme, tetraglyme, 1,2-dimethoxyethane, 1,2-diethoxyethane 1-ethoxy, 2-methoxyethane, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, ethyl methyl carbonate, methyl propyl carbonate, ethyl propyl carbonate, or mixtures thereof.
- 15 10. The electrochemical cell according to any one of Claims 1 to 9 wherein the second solvent is selected from propylene carbonate, ethylene carbonate, butylene carbonate, acetonitrile, dimethyl sulfoxide, dimethyl formamide, dimethyl acetamide, γ -butyrolactone, N-methyl-pyrrolidinone, or mixtures thereof.
- 20 11. The electrochemical cell according to any one of Claims 1 to 10 wherein the alkali metal salt is selected from LiPF₆, LiBF₄, LiAsF₆, LiSbF₆, LiClO₄, LiAlCl₄, LiGaCl₄, LiC(SO₂CF₃)₃, LiN(SO₂CF₃)₂, LiSCN, LiO₃SCF₂CF₃, LiC₆F₅SO₃, LiO₂CF₃, LiSO₃F, LiB(C₆H₅)₄, LiCF₃SO₃, or mixtures thereof.
- 25 12. The electrochemical cell according to any one of Claims 1 to 11 wherein the solid cathode is selected from silver vanadium oxide, copper silver vanadium oxide, manganese dioxide, cobalt oxide, nickel oxide, fluorinated carbon, copper oxide, copper sulfide, iron sulfide, iron disulfide, titanium disulfide, copper vanadium oxide, or mixtures thereof.
- 30 13. The electrochemical cell according to any one of Claims 1 to 12 wherein the anode is comprised of lithium or a lithium-aluminum alloy.
14. The electrochemical cell according to any one of Claims 1 to 13 wherein the cathode comprises from about 80 to about 99 weight percent of the cathode active material.
- 35 15. The electrochemical cell according to any one of Claims 1 to 15 wherein the cathode further comprises a binder material and a conductor additive.
16. The electrochemical cell according to Claim 15 wherein the binder material is a fluoro-resin powder.
- 40 17. The electrochemical cell according to Claim 15 or Claim 16 wherein the conductive additive is selected from carbon, graphite powder or acetylene black or metallic powder selected from titanium, aluminum, nickel, stainless steel, or mixtures thereof.
- 45 18. The electrochemical cell according to any one of Claims 1 to 17 wherein the cathode comprises from about 0 to 3 weight percent carbon, about 1 to 5 weight percent of a powder fluoro-resin and about 94 weight percent of the cathode active material.
- 50 19. The electrochemical cell according to any one of Claims 1 to 18 wherein the cathode includes a mixed metal oxide comprised of vanadium oxide and a second metal "SM" selected from Groups IB, IIB, IIIB, IVB, VIB, VIIB and VIII of the Periodic Table of the Elements, the mixed metal oxide having the general formula SM_xV₂O_y wherein 0.30 ≤ x ≤ 2.0 and 4.5 ≤ y ≤ 6.0.
- 55 20. The electrochemical cell according to any one of Claims 1 to 18 wherein the cathode includes a mixed metal oxide comprised of vanadium oxide and a mixture of copper and a second metal "SM" selected from Groups IB, IIB, IIIB, IVB, VIB, VIIB and VIII of the Periodic Table of the Elements, the mixed metal oxide having the general formula Cu_xSM_yV₂O_z wherein 0.01 ≤ x ≤ 1.0, 0.01 ≤ y ≤ 1.0 and 5.01 ≤ z ≤ 6.5.

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21. The electrochemical cell according to Claim 20 wherein the general formula $x \leq y$.
22. An unplantable medical device comprising the electrochemical cell according to any one of Claims 1 to 21.
- 5 23. The implantable medical device according to Claim 22 wherein the device requires at least one current pulse for a medical device operating function.
24. A method for reducing voltage delay in the pulse discharging electrochemical cell according to any one of Claims 1 to 21 activated with a nonaqueous electrolyte, comprising the steps of:
- 10 a) providing an anode comprising an alkali metal;
b) providing a solid cathode of electrically conductive material;
c) activating the electrochemical cell with the nonaqueous electrolyte operatively associated with the anode and the cathode, the nonaqueous electrolyte comprising:
- 15 i) a first solvent selected from the group consisting of an ester, an ether and a dialkyl carbonate, and mixtures thereof;
ii) a second solvent selected from the group consisting of a cyclic carbonate, a cyclic ester and a cyclic amide, and mixtures thereof;
20 iii) a phosphonate additive; and
iv) an alkali metal salt dissolved therein, wherein the alkali metal of the salt is similar to the alkali metal comprising the anode; and
- 25 d) discharging the cell to deliver at least one current pulse of a short duration burst of electrical current of a significantly greater amplitude than that of a prepulse current immediately prior to the pulse such that the pulse one end potential minus the pulse one minimum potential is less than about 0.3 volts.
25. A method of powering an implantable medical device wherein the device comprises the electrochemical cell according to any one of Claims 1 to 21 or wherein the device comprises the electrochemical cell made using the method according to Claim 24.
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EUROPEAN SEARCH REPORT

Application Number
EP 98 30 8689

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<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>			

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